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Phase Transition in Small System

Ph. Chomaz[1], F. Gulminelli[2*]
[1] GANIL, DSM-CEA/IN2P3-CNRS,
BP 5027, F-14076 CAEN cedex 5, FRANCE
[2] LPC Caen, IN2P3-CNRS et Université,
F-14050 CAEN cedex, FRANCE

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Everybody knows that when a liquid is heated, its temperature increases until the moment when it starts to boil. The increase in temperature then stops, all heat being used to transform the liquid into vapor. What is the microscopic origin of such a strange behavior? Does a liquid drop containing only few molecules behave the same? Recent experimental and theoretical developments seem to indicate that at the elementary level of very small systems, this anomaly appears in an even more astonishing way: during the change of state - for example from liquid to gas - the system cools whereas it is heated, i.e. its temperature decreases while its energy increases. This paper presents a review of our understanding of the negative specific heat phenomenon.

1. Introduction

Phase transitions are universal phenomena which have been theoretically understood at the thermodynamic limit of infinite systems as anomalies in the associated equation of state (EoS). They have been classified according to the degree of non-analyticity of the thermodynamic potential at the transition point. As an example figure 1 shows a first order phase transition i.e. a jump in the average energy $< E >= -\partial_\beta \log Z_\beta$, Z_β being the canonical partition sum, as a function of the conjugate intensive variable β.

However, most of the systems studied in physics do not correspond to this mathematical limit of infinite systems[?] and, in fact, finite systems are now, per se, a subject of a very intense research activity, from metallic clusters[?, ?] to Bose condensates[?, ?], from nanoscopic systems[?] to atomic nuclei [?] and elementary particles[?].

2. Finite systems

The thermodynamic potentials of a finite system in a finite volume are analytic functions. As a consequence, the average energy varies continuously with the temperature and cannot present a jump. The transition looks like a crossover (see fig. 1). Thus, it is often concluded that phase transitions can only be defined for infinite systems. This situation can be thought as unsatisfactory, since on one hand the thermodynamic limit

*member of the Institut Universitaire de France

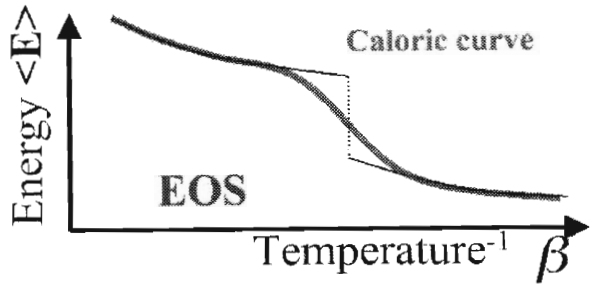

Figure 1. Canonical caloric curve $< E >= -\partial_\beta \log Z_\beta$ presenting a discontinuity characteristic of a first order phase transition for an infinite system (thin line) while it remains continuous in a finite system (thick line).

does not exist in nature, and on the other hand the understanding of mesoscopic systems is becoming one of the most challenging field in physics [?].

In the recent years, many efforts have been devoted to give the theoretical foundations for the definition of phase transitions in small systems and explicitly make the bridge between possible anomalies in finite systems and the usual definition of phase transitions at the thermodynamical limit [?].

2.1. Phase transition in the intensive ensembles: Zeroes of $\log Z$ and bimodality of the event distribution.

Following Yang and Lee[?] ideas, a classification scheme valid for finite systems has been proposed by Grossmann [?] using the distribution of zeroes of the canonical partition sum in the complex temperature plane (see top of fig. 2). Alternatively, we have recently proposed the possible bimodality of the probability distribution of observable quantities as a direct definition of a phase transition [?] (see fig. 2), the direction separating the two phases being an order parameter.

A typical example, the distribution of the magnetization of the 3D Ising model, is shown in figure 3. The observed bifurcation is characteristic of a second order phase transition. Below the critical point the bimodality in the magnetization transition indicates a first order transition at finite magnetic field (the intensive variable conjugated to the magnetization).

In a recent work[?] we have demonstrated that this definition of phase transitions in finite systems based on bimodality is consistent with the Yang Lee theorem [?], *i.e.* with the standard definition of first order phase transitions in the thermodynamic limit. The first step is to make the link between the partition sum and the event distribution. Taking the example of a canonical ensemble both quantities are directly related to the density of states $W(E) : P_\beta(E) = W(E)e^{-\beta E}/Z_\beta$ and $Z_\beta = \int W(E)e^{-\beta E}dE$. Therefore, introducing a reference temperature β_0 we get

$$Z_\beta = Z_{\beta_0} \int P_{\beta_0}(E)e^{-(\beta-\beta_0)E}dE \tag{1}$$

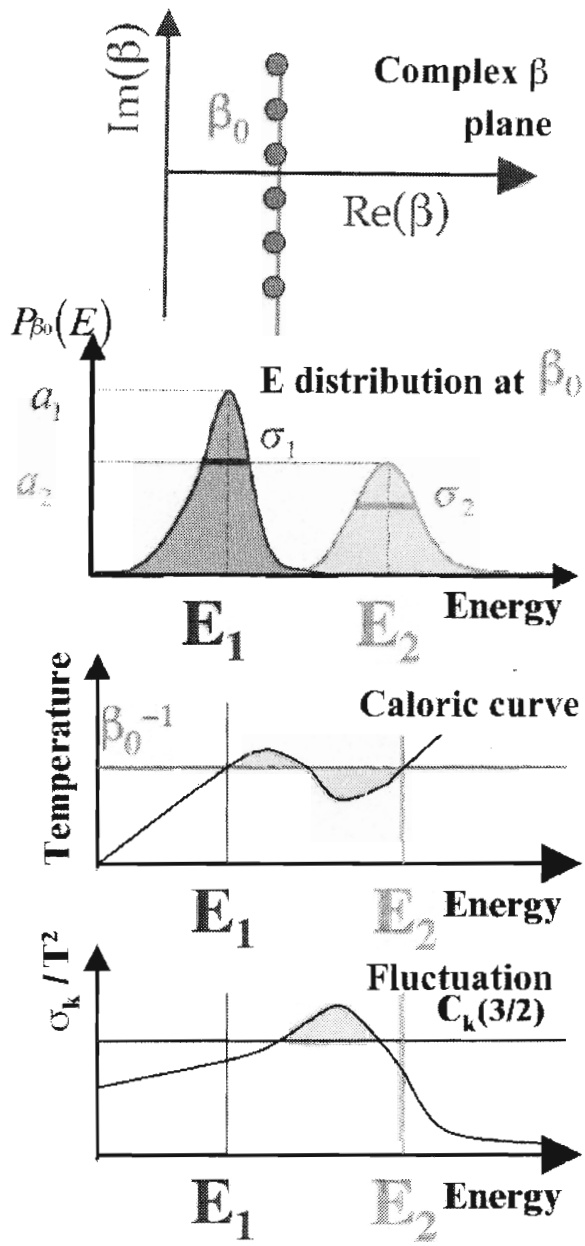

Figure 2. Various equivalent definitions of a first order phase transition in a finite system: an alignment of the zeroes of the partition sum in the complex temperature plane (top); a bimodality of the event distribution (below); a negative heat capacity (below) and an abnormal kinetic energy fluctuation (bottom).

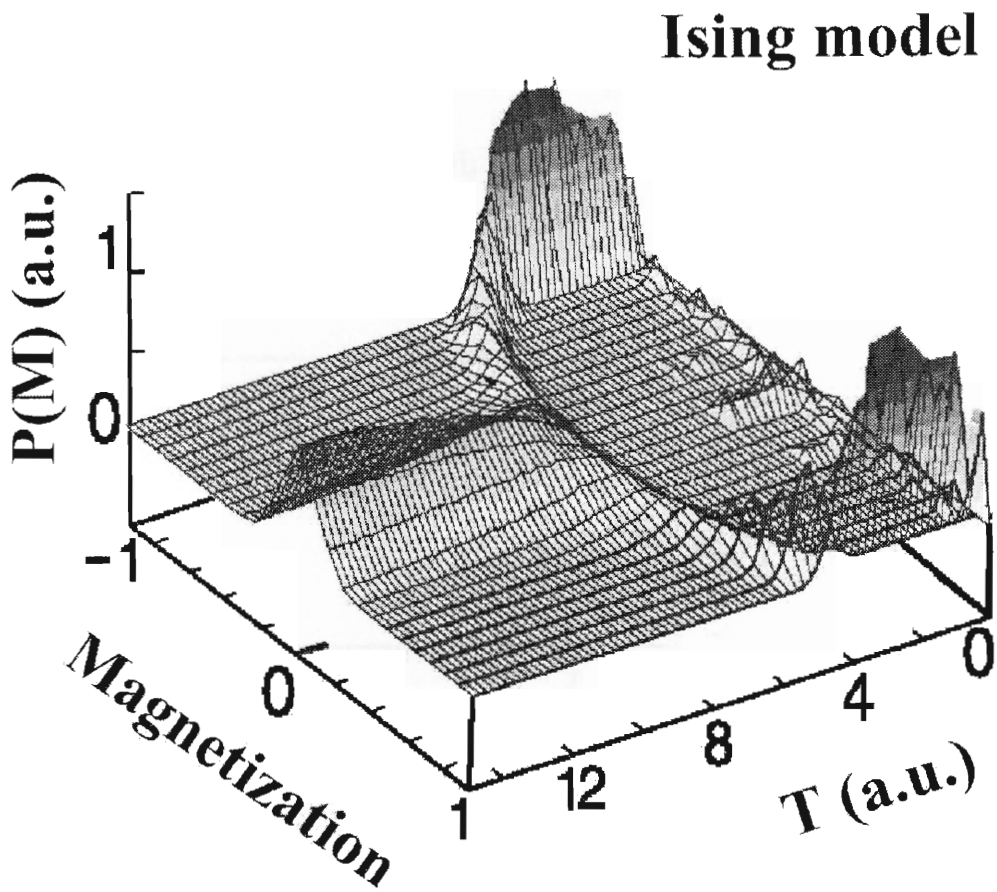

Figure 3. Evolution of the magnetization distribution as a function of the temperature in the Ising model ($\varepsilon/2$ is the strength of the spin spin interaction)

i.e. the partition sum is the Laplace transform of the event distribution. A single distribution $P_{\beta_0}(E)$ at a given temperature β_0) is in principle enough to reconstruct the whole partition sum for all temperatures β. This is only true for finite systems since at the thermodynamic limit the distribution P becomes a delta function which contains information only about the temperature β_0 (as required by the theorem of ensembles equivalence).

Using (**??**) one can show that a set of zeroes converging and aligning perpendicularly to the reel temperature axis, as required by the Yang-Lee theorem, is equivalent to a probability distribution split at least in 2 equivalent components (bimodal), separated by an energy inversely proportional to the density of zeroes close to the real axis, *i.e.* directly proportional to the number of particles A. The resulting finite energy jump per particle is the latent heat.

2.2. Link between intensive and extensive ensembles:

Bimodality of the event distribution and negative heat capacity.

Alternative definitions of phase transitions in finite systems have been proposed. It has been claimed that first order phase transitions in finite systems can be related to a negative microcanonical heat capacity [**?**, **?**] or more generally to an inverted curvature of the thermodynamic potential as a function of an observable which can then be seen as an order parameter [**?**]. These anomalies can also be connected to the general topology of the potential energy surface [**?**].

It should be noticed that this definition of phase transitions can be used only in an ensemble in which an extensive variable[**?**] playing the role of an order parameter is controlled (extensive ensemble) since it is based on the curvature anomalies of the associated thermodynamical potential as a function of the controlled extensive variable. Conversely, both the Yang-Lee and the bimodality pictures require that the extensive variables are not directly controlled but are free to fluctuate being constrained only by a Lagrange multiplier . This corresponds to the associated intensive ensemble. In this sense definitions based on negative curvatures or on bimodalities (or on the zeroes of the partition sum) are complementary, since they cannot be applied to the same ensemble.

We have demonstrated that these two pictures are equivalent and are the manifestation of the same phenomenon in two different ensembles[**?**]. This can be easily demonstrated. Let us take the energy as a typical extensive variable. The inverted curvature definition of a first order phase transition is nothing but the occurrence of a negative heat capacity in the microcanonical ensemble, while the bimodality should be looked for in the canonical energy distribution. However, using the definition of the microcanonical entropy $S(E) = \log W(E)$ and of the canonical energy distribution $P_\beta(E)$ one can directly show that they are intimately related by the equality

$$\log P_\beta(E) = S(E) - \beta E - \log Z_\beta \tag{2}$$

The above relation is valid for every temperature β^{-1} and every energy E, meaning that in a finite system the energy probability a single temperature is in principle enough to access the whole entropy functional. However, from a practical point of view enough statistics should be accumulated in a given energy bin in order to infer the associated entropy so that Eq. (**??**) can be used in practice only in the strongly populated region.

From Eq. (??) it is clear that the curvature of $\log P_\beta(E)$ is directly the curvature of S. Then, a bimodal probability distribution implies a negative heat capacity and, vice versa, a negative entropy curvature leads to a bimodal energy distribution for an canonical temperature β equal to the microcanonical one at the maximum of the curvature inversion.

An illustration of the relation between the signal of phase transition in various ensembles in the case of an isobar Lattice-gas model[?] is presented in figure ??. In the top figure obtained in the canonical ensemble, the log of the energy distributions is presented. The calculation is performed close to the transition temperature, and the distribution is bimodal as expected. Because of eq. (??) this figure also represents the entropy (with a linear behavior $\beta E + \log Z_\beta$ subtracted); its derivative is the microcanonical temperature $T^{-1} = \partial_E S = \beta + \partial_E P_\beta$ and its curvature the inverse of a heat capacity $C^{-1} = 1/\partial_E T = -T^2 \partial_{EE} S = -T^2 \partial_{EE} P_\beta$. The bimodality is nothing but a convex intruder in the entropy curve, which produces a back bending in the microcanonical caloric curve and a negative branch in the heat capacity (see figure ??).

For comparison on the microcanonical caloric curve of fig. (??) we also present the canonical average and most probable energies. In the back-bending the canonical distribution is bimodal so that the most probable energy is discontinuous (big dots) and so is presenting the energy jump characteristic of a first order phase transition. Conversely the usual canonical caloric curve which relates the average energy to the temperature takes the whole back bending region (i.e. the whole range of temperatures exhibiting a bimodal energy distribution) to go smoothly from the gas to the liquid (dotted line).

2.3. Partitioning of energy and microcanonical entropy

Negative heat capacity and abnormal kinetic energy fluctuations.

In ref. [?] we have proposed to use the fluctuations of the kinetic energy to deduce the microcanonical heat capacity and we have shown that a negative heat capacity results in an abnormally large energy fluctuation. This can be easily explained for a classical fluid and tested in the framework of the lattice-gas model. The total energy E of the considered system can be decomposed into two independent components, its kinetic and potential energy: $E = K + V$. In a microcanonical ensemble with a total energy E the total degeneracy factor $W(E) = \exp(S(E))$ is thus simply given by the folding product of the individual degeneracy factors $W_k(K) = \exp(S_k(K))$ and $W_v(V) = \exp(S_v(V))$. One can then define for the total system as well as for the two subsystems the microcanonical temperatures T_i and the associated heat capacities C_i (with $i = k$ or v). If we now look at the kinetic energy distribution when the total energy is E we get

$$P_E(K) = \exp(S_k(K) + S_v(E - K) - S(E)) \tag{3}$$

Then the most probable kinetic energy $\bar{K}_E$ for the total energy E is defined by the equality of the partial microcanonical temperatures $T_k(\bar{K}_E) = T_v(E - \bar{K}_E)$. The most probable kinetic energy $\bar{K}_E$ can be used as a microcanonical thermometer. Using a Gaussian approximation for $P_E(K)$ the kinetic energy variance can be calculated as [?]

$$\sigma_k^2 = \bar{T}^2 \frac{C_k C_v}{C_k + C_v} \tag{4}$$

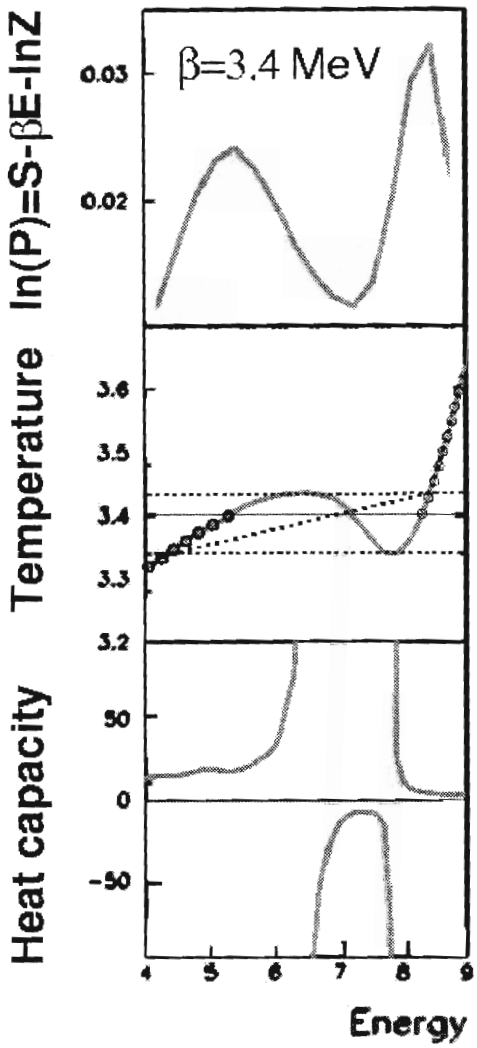

Figure 4. Top: log of the energy distribution (a little above the transition temperature) which is nothing but the entropy except for a subtracted linear behavior. Middle: the deduced microcanonical temperature. For comparison the canonical caloric curve $< E >$ as a funtion of β^{-1} as well as the most probable energy are also plotted (dotted line and big dots respectively). Bottom: the associated microcanonical heat capacity.

where C_k and C_v are the microcanonical heat capacities calculated for the most probable energy partition. Equation (**??**) can be inverted to extract from the observed fluctuations the heat capacity

$$C \simeq C_k + C_v = \frac{C_k}{1 - \sigma_k^2/\bar{\sigma}_k^2} \tag{5}$$

where we have introduced the canonical kinetic energy fluctuation $\bar{\sigma}_k^2 = \bar{T}^2 C_k$. This expression shows that when C_v diverges and then becomes negative, σ_k^2 remains positive but overcomes the canonical expectation $\bar{\sigma}_k^2 = \bar{T}^2 C_k$. This anomalously large kinetic energy fluctuation is a signature of the first order phase transition.

The normalized fluctuations $\sigma_K^2/{T_\lambda}^2$ obtained in the microcanonical ensemble for a lattice-gas with an average volume constrained by a Lagrange multiplier λ are shown in the energy-λ plane in figure **??** together with the isotherms. One can clearly see that the fluctuations are abnormally large in the coexistence region up to the critical temperature. From fig. **??** it is apparent that the phase transition signal is visible in the temperature (back-bending) as well as in the fluctuation observable (normalized fluctuations larger than C_k).

The right part of the figure presents examples of expected behavior of the temperature as a function of energy at a constant pressure or a constant average volume in the subcritical region. At constant pressure a back-bending is clearly seen. On the other hand at constant average volume a smooth behavior is observed with a slope change entering the gas phase. This is due to the fact that the λ parameter varies rapidly in the coexistence region. From these examples one clearly sees that the various transformations lead to very different caloric curves. More generally, it is clear that the back-bending of the temperature surface can be avoided depending on the path of the considered transformation and the phase transition signal can be hidden in the observation of the caloric curve.

On the other side partial energy fluctuations are a state variable which does not depend on the transformation from one state to another and can directly give access to the equation of state: the anomalously large fluctuation signal will be always seen if the system undergoes a first order phase transition, independent of the path. As an example the lower part of figure 5 shows a constant P_λ or $< V >_\lambda$ cut of the bidimensional fluctuation surface. The quantitative behavior of the heat capacity as a function of energy depends on the specific transformation, but at each point the heat capacity extracted from fluctuations is a direct measure of the underlying equation of state. This is clearly demonstrated in the medium part of figure **??** which compares the exact heat capacity C_λ with the fluctuation approximation. The agreement between the two results illustrates the accuracy of the estimation (14).

3. Conclusions

Phase transitions are universal properties of matter in interaction. They have been widely studied in the thermodynamical limit of infinite systems. However, in many physical situations this limit cannot be accessed and so phase transitions should be reconsidered from a more general point of view. This is for example the case of matter under long range

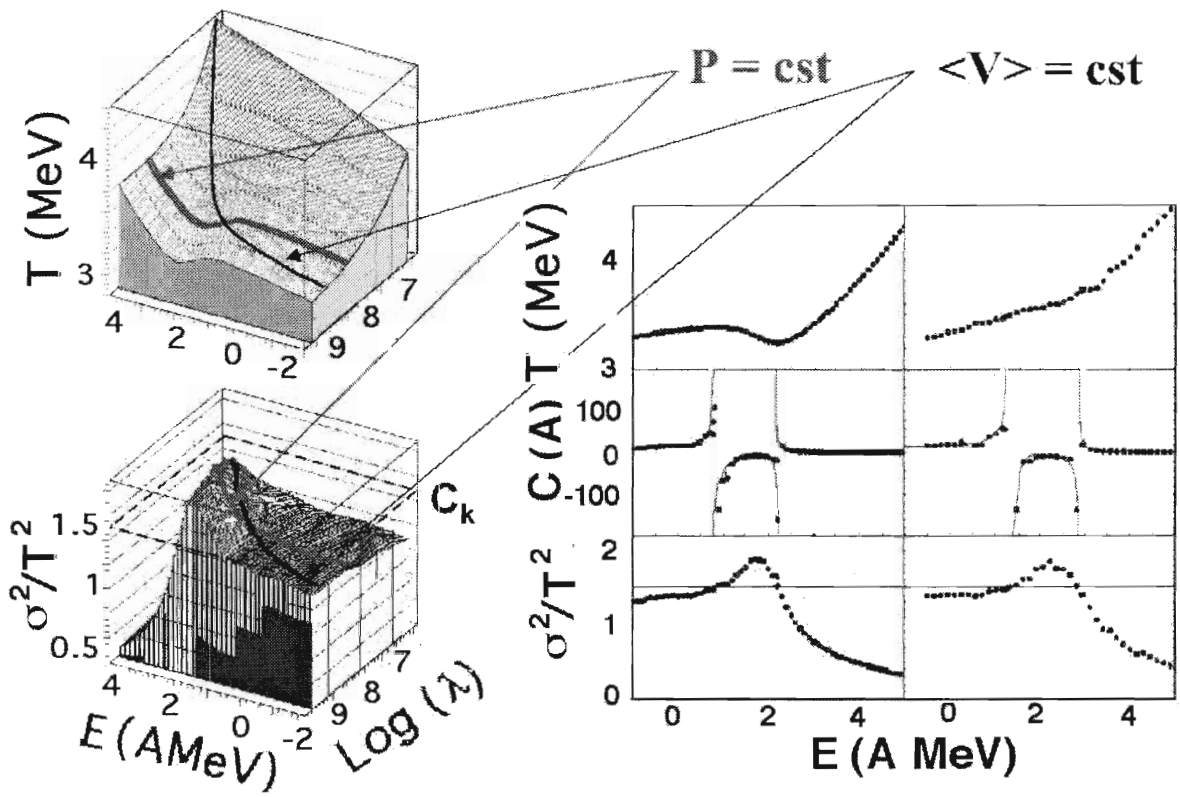

Figure 5. Isobar lattice gas model: Left part : Isotherms and contour plot of the normalized kinetic energy fluctuations in the Lagrange parameter versus energy plane. The level corresponding to the canonical expectation $\sigma_1^2/T^2 = 1.5$ is shown. Thick line: critical isotherm. Right panel : Thermodynamic quantities in the microcanonical ensemble for a transformation at constant pressure and at constant volume (right part). Upper panels: caloric curve. Lower panels: normalized kinetic energy fluctuations compared to the canonical expectation (lines). Medium panels: heat capacity (symbols) compared to the estimation through eq.(5) (lines) at constant pressure (left part) and at constant volume (right part).

forces like gravitation. Even if these self gravitating systems are very large they cannot be considered as infinite because of the non saturating nature of the force. Other cases are provided by microscopic or mesoscopic systems built out of matter which is known to present phase transitions. Metallic clusters can melt before being vaporized. Quantum fluid may undergo Bose condensation or super-fluid phase transition. Dense hadronic matter should merge in a quark and gluon plasma phase while nuclei are expected to exhibit a liquid -gas phase transition. For all these systems the theoretical and experimental issue is how to sign a possible phase transition in a finite system.

In this paper we have shown that phase transitions can be uniquely defined for finite systems. Depending upon the statistical ensemble one should look for different signals. In the ensemble where the order parameter is free to fluctuate (intensive ensemble) the topology of the event distribution should be studied. A bimodal distribution signals a first order phase transition. This occurrence of a bimodal distribution is equivalent to the alignment of the partition sum zeroes as described by the Yang and Lee theorem. In the associated extensive ensemble, the bimodality condition is equivalent to the requirement of a convexity anomaly in the thermodynamic potential.

The first experimental evidences of such a phenomenon have been reported recently different fields: the melting of sodium clusters[?], the fragmentation of hydrogen clusters[?], the pairing in nuclei[?] and nuclear multifragmentation[?]. However, much more experimental and theoretical studies are now expected to progress in this new field of phase transitions in finite systems.

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